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INFLUENCE OF THE ELECTROCHEMICAL ANODIZING PARAMETERS ON THE MICROSTRUCTURE, MICROROUGHNESS AND MICROHARDNESS OF ANODIZED Ti-6Al-7Nb

This paper presents a study on anodizing titanium alloy Ti-6Al-7Nb in electrolyte of dilute sulfuric acid. The effects of the parameters – voltage, anodizing time, and electrode distance on the anodic film properties have been investigated. The anodic layers are found to become more compact with the increase of the applied voltage in the electrolytic cell. The microstructure, chemical element distribution and mechanical properties, i.e. microroughness and microhardness of the anodic coatings obtained at different operating conditions have been evaluated.

Keywords: anodizing, surface oxidation, electrochemical, titanium alloy, Ti-6Al-7Nb

1. Introduction

The electrochemical anodizing is a common surface modification method for Ti and its alloys where the work piece is used as anode in an electrolytic cell to form stable oxide coating [1-8]. The process can be performed under potentiostatic or galvanostatic mode in numerous electrolytes. Its purpose is increasing the performance of the anodized surface [9-12]. This process allows the oxide layer to obtain various desired properties by controlling the electrochemical parameters, such as electrolyte composition and concentration, applied potential or current, temperature, etc. [13-15].

This paper presents preliminary results of the study on anodizing titanium alloy Ti-6Al-7Nb. The influence of the anodizing process parameters (voltage, anodizing time and distance between the electrodes) on the microstructure, element distribution, microroughness and microhardness is investigated in particular.

2. Experimental

In preparation for anodizing, cylindrical samples having a diameter of 12 mm and 4 mm length were processed by mechanical grinding, chemical degreasing and deoxidation. The specimens are made of commercially available Ti-6Al-7Nb. The chemical composition of the used alloy is according to ISO 5832-11. The samples prepared were anodized electrochemically in 1M sulfuric acid solution at various voltage, time and electrode distance.

Microstructure examination is performed on Hitachi S-4700 SEM. The element distribution is measured by energy dispersive spectroscopy (EDS, Joel, JSM 6060-LU). Microroughnes results are obtained using roughness measuring instrument – Marsurf PS10. The microhardness of the anodized samples is measured by the Vickers apparatus HVS-1000 with applied load of 0.01 kg.

3. Results and discussion

3.1. Microstructure analysis

The study on electrochemical anodizing shows that the process parameters are directly related to the microstructure and the mechanical properties of the oxide layers formed on titanium alloy Ti-6Al-7Nb. The microstructure of the anodic oxides appears to be non-uniform and porous (Fig. 1). Micro cracks are most likely to occur as a result of internal stresses during the oxide layer growth. As the thickness of the layer increase, the micro cracks tend to decrease. The microstructural analysis indicates that an increase of the voltage, between 10 V and 100 V, results in more compact structure and higher density of the oxide layer (Fig. 2).

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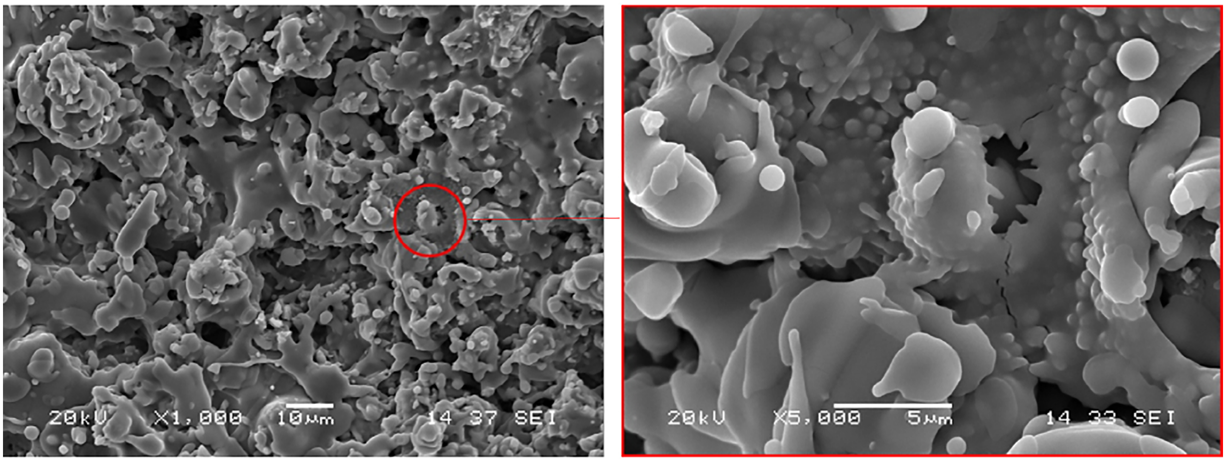

Fig. 1. SEM images of anodized Ti-6Al-7Nb specimens in 1M H2SO4 at 10 V

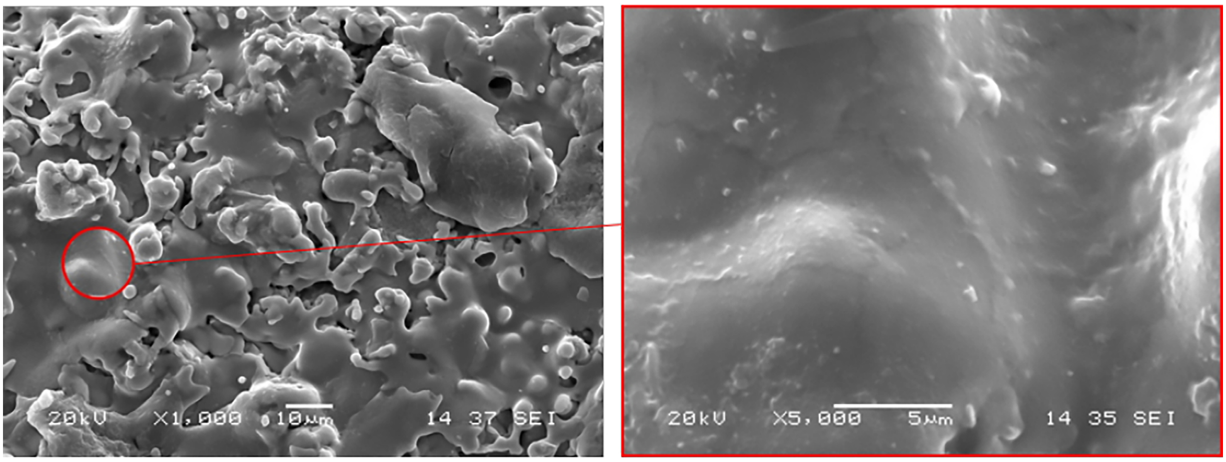

Fig. 2. SEM images of anodized Ti-6Al-7Nb specimens in 1M H2SO4 at 100 V

3.2. EDS analysis

The chemical element distribution on the surface is of great importance for the properties of the processed parts. The analysis of the results indicates that titanium and oxygen are present on the surface to form an oxide layer with dimensions up to 200 nm. Near the surface, the concentration of the alpha and beta alloying elements is decreasing. In-depth the oxygen content is decreasing and the presence of aluminum and niobium increase (Fig. 3, Table 1-3). This effect can be explained by the higher activity of titanium to oxygen.

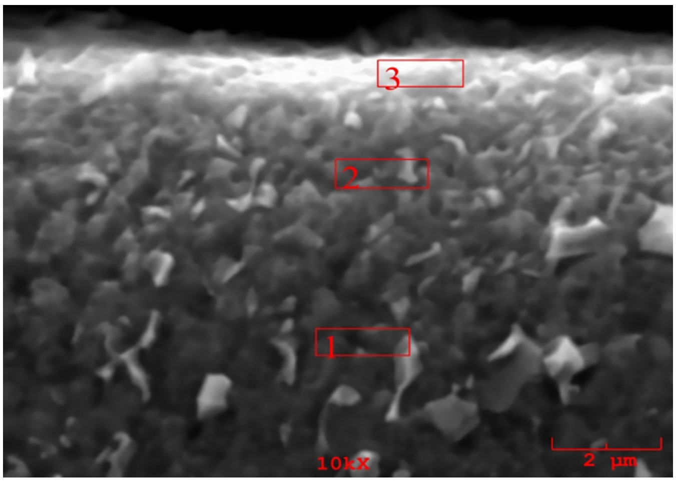

Fig. 3. Microstructure and testing zones of electrochemically anodized Ti-6Al-7Nb at voltage – 100 V, time – 30 sec. and electrode distance – 100 mm

TABLE 1

Chemical elements distribution in zone 1

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
Al	Ka	44.57	4.22	7.779	wt.%
Ti	Ka	465.58	13.645	85.43	wt.%
Nb	La	28.13	3.354	6.801	wt.%

TABLE 2

Chemical elements distribution in zone 2

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	4.39	1.325	9.521	wt.%
Al	Ka	51.88	4.555	8.529	wt.%
Ti	Ka	436.99	13.219	76.262	wt.%
Nb	La	24.17	3.109	5.688	wt.%

TABLE 3

Chemical elements distribution in zone 3

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
C	Ka	37.93	3.895	19.692	wt.%
O	Ka	18.23	2.7	22.893	wt.%
Al	Ka	74.57	5.461	8.677	wt.%
Ti	Ka	338.81	11.64	45.365	wt.%
Nb	La	17.95	2.679	3.373	wt.%

3.3. Microroughness analysis

The results obtained from the conducted study on electrochemical anodizing Ti-6Al-7Nb illustrate the influence of the technological parameters of the regime, within the limits of their range in the study on the microroughness values Ra and Rz. Table 4 lists the minimum and maximum values obtained for Ra and Rz as well as the trend for each controlled parameter i.e X1 – voltage, X2 – time and X3 – electrode distance.

After analyzing the results, it was established:

- Ra ranges from 0.038 µm to 0.302 µm.
- The highest value of Ra is obtained at voltage – 100 V, time – 90 s and electrode distance – 200 mm.
- Ra has lowest value at 10 V, 57 s and electrode distance of 200 mm.
- As the voltage increases, Ra increases.
- By increasing the anodizing time between 30 s and 57 s Ra decreases; from 57 to 90 s Ra increases.
- By increasing the distance between the electrodes from 100 mm to 150 mm there is an increase in Ra; from 150 mm to 200 mm Ra decreases.
- Rz varies in the range of 0.105 µm-2.332 µm.
- Maximum value of Rz is obtained at 100 V, 30 s and electrode distance of 200 mm.
- As the voltage increases, Ra increases.
- Lowest value for Rz is obtained at 10 V, 57 s and electrode distance of 200 mm.
- By increasing the anodizing time between 30 and 57 s, Rz decreases; from 57 s to 90 s Rz increases.
- At 10 V by increasing the distance between the electrodes from 100 mm to 150 mm Rz increases; Rz decrease from 150 mm to 200 mm.

3.4. Microhardness analysis

The microhardness data for the anodized specimens is obtained by the average of three measurements for each, followed by a regression analysis. The analysis resolution is used to build a dynamic three dimensional chart (Fig. 4).

The data analysis indicates:

- The microhardness varies between 291 HV – 900 HV.
- The highest microhardness value is obtained at 100 V, 90 s and electrode distance of 200 mm.
- The lowest microhardness value is obtained at 28 V, 48 s and 100 mm electrode distance.
- As the distance between the electrodes increases, the microhardness increases.
- The microhardness increases significantly with the increase of the voltage from 10 to 100 V
- By increasing the anodizing time, between 30 s and 50 s the microhardness decreases. The microhardness is increasing from 50 s to 90 s.

4. Conclusion

The Ti-6Al-7Nb specimens were anodized in a dilute sulfuric acid electrolyte. The effects of various voltage, anodizing time and distance between the electrodes have been investigated. The main conclusions of this study are given below.

(1) The microstructure, formed during the electrochemical anodization process, develops into more compact and denser layer with the increase of the voltage from 10 V to 100 V.

(2) Micro cracks are observed. They are most likely to occur due to internal stresses during the oxide layer growth.

(3) The EDS analysis indicates the presence of titanium and oxygen, which form an oxide layer with dimensions up to 200 nm. The concentration of alpha and beta alloying ele-

TABLE 4

Trends and of the surface microroughness parameters Ra and Rz after electrochemical anodization of Ti-6Al-7Nb

	Ra												Trend
	-1				0				1				
X1	MIN=	0.039	MAX=	0.171	MIN=	0.050	MAX=	0.222	MIN=	0.052	MAX=	0.302	
X2	MIN=	0.116	MAX=	0.294	MIN=	0.040	MAX=	0.205	MIN=	0.136	MAX=	0.302	
X3	MIN=	0.050	MAX=	0.155	MIN=	0.058	MAX=	0.151	MIN=	0.039	MAX=	0.302	
	Rz												Trend
	-1				0				1				
X1	MIN=	0.413	MAX=	2.198	MIN=	0.702	MAX=	2.506	MIN=	0.995	MAX=	3.859	
X2	MIN=	1.177	MAX=	3.859	MIN=	0.422	MAX=	2.612	MIN=	1.559	MAX=	3.257	
X3	MIN=	0.682	MAX=	2.244	MIN=	0.834	MAX=	2.544	MIN=	0.413	MAX=	3.856	

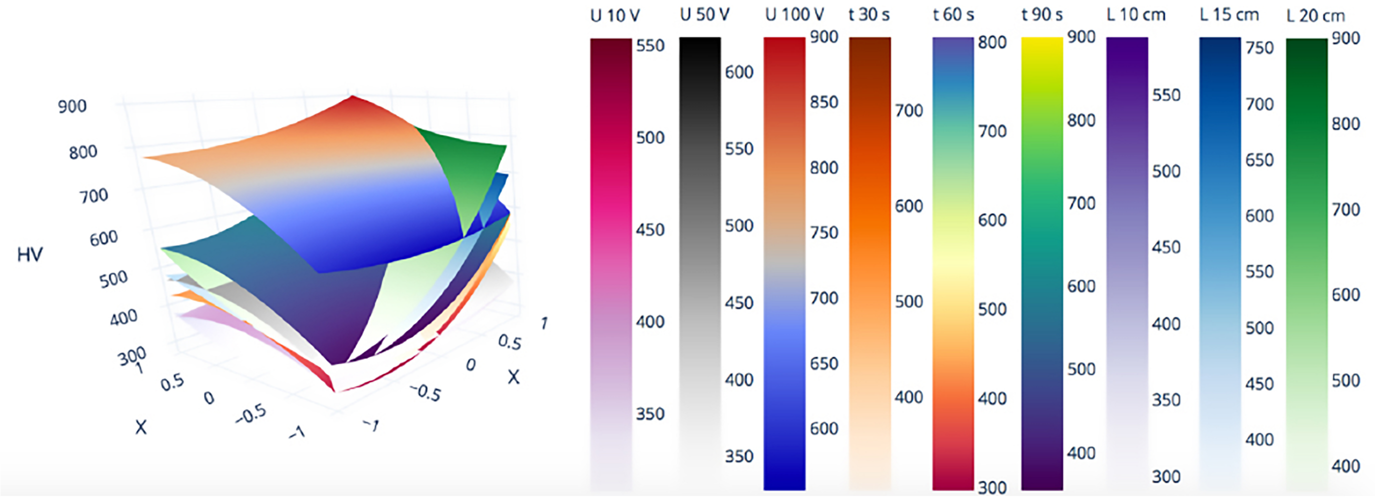

Fig. 4. Influence of the anodizing voltage (U), time (t) and electrode distance (L) on the surface microhardness (HV)

ments in the alloy decreases near the surface. The oxygen content is reduced in-depth and the presence of aluminum and niobium increases. This effect is explained with the higher activity of titanium to oxygen.

(4) Graphical analysis of the surface roughness (for the parameters Ra and Rz) and the voltage parameters (U, V), the anode time (t, s), and the distance between the electrodes (L, mm) has been conducted. Data arrays have been created to observe the variations of Ra and Rz when changing the values of the technological parameters from –1 to +1. The influence of the particular technological parameters on the surface roughness has been determinated.

(5) Graphical analysis of the microhardness (HV) and the voltage parameters (U, V), the anode time (t, s), and the distance between the electrodes (L, mm) has been conducted. Data arrays have been created to observe the microhardness alterations when changing the values of the technological parameters from –1 to +1. The influence of the particular technological parameters on the microhardness has been determinated.

REFERENCES

[1] S.D. Cramer, B.S. Covino, Corrosion: Fundamentals, Testing, and Protection **13A**, (2003), ASM International, ISBN: 978-0871707055.

[2] N. Lowrie, Surface Treatment of Titanium: A Designers and Users Handbook, Titanium Information Group, (2006), ISBN: 978-0-9553136-0-8.

[3] J.L. Delplancke, M. Degrez, A. Fontana, R. Winand, Influence of the anodizing procedure on the structure and the properties of titanium oxide films and its effect on copper nucleation, Electrochimica Acta **39**, 8-9, 1281-1289 (1994).

[4] M.V. Diamanti, M.P. Pedeferri, The Anodic Oxidation of Titanium and Its Alloys, Encyclopedia of Interfacial Chemistry, Elsevier, 41-54 (2018).

[5] Xinwen Huang, Zongjian Liu, Growth of titanium oxide or titanate nanostructured thin films on Ti substrates by anodic oxidation in alkali solutions, Surface and Coatings Technology **232**, 224-233 (2013).

[6] İlhan Çelik, Akgün Alsaran, Gencaga Purcek, Effect of different surface oxidation treatments on structural, mechanical and tribological properties of ultrafine-grained titanium, Surface and Coatings Technology **258**, 842-848 (2014).

[7] H.D. Traid, M.L. Vera, A.E. Ares, M.I. Litter, Porous Titanium Dioxide Coatings Obtained by Anodic Oxidation for Photocatalytic Applications, Procedia Materials Science **9**, 619-626 (2015).

[8] A. Aladjem, J. Mater. Sci. **8**, 688 (1973).

[9] C. Casado, S. Mesones, C. Adán, J. Marugán, Comparing potentiostatic and galvanostatic anodization of titanium membranes for hybrid photocatalytic/microfiltration processes, Applied Catalysis A: General **578**, 40-52 (2019).

[10] E. Mena, M.J. Martín de Vidales, S. Mesones, J. Marugán, Influence of anodization mode on the morphology and photocatalytic activity of TiO2-NTs array large size electrodes, Catalysis Today **313**, 33-39 (2018).

[11] E. Mena, M. López, M.J. Martín de Vidales, J. Marugán, Modeling the anodization of large titanium electrodes, Chemical Engineering Science **186**, 74-83 (2018).

[12] Maoying Liao, Hongtu Ma, Dongliang Yu, Hua Han, Xuran Xu, Xufei Zhu, Formation mechanism of anodic titanium oxide in mixed electrolytes, Materials Research Bulletin **95**, 539-545 (2017).

[13] D.J. Blackwood, L.M. Peter, The influence of growth rate on the properties of anodic oxide films on titanium, Electrochimica Acta **34**, 11, 1505-1511(1989).

[14] A.C. Alves, F. Wenger, P. Ponthiaux, J.-P. Celis, A.M. Pinto, L.A. Rocha, J.C.S. Fernandes, Corrosion mechanisms in titanium oxide-based films produced by anodic treatment, Electrochimica Acta **234**, 16-27 (2017).

[15] Tingting Wang, Lina Wang, Qianqian Lu, Zhen Fan, Changes in the esthetic, physical, and biological properties of a titanium alloy abutment treated by anodic oxidation, The Journal of Prosthetic Dentistry**121**, 1, 156-165 (2019).